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STRUCTURE OF OXYGLUTINOSONE AND EPIOXYLUBIMIN, STRESS METABOLITES FROM DISEASED POTATO TUBERS1)

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The structure of oxyglutinosone and epioxylubimin, stress metabolites isolated from diseased potato tubers, was determined to be formulas **1** and **2** on the basis of the chemical and spectral evidence.

In a continuing study on phytoalexins produced by tuber tissues of potatoes (*Solanum tuberosum* × *S. demissum*) infected by an incompatible race of *Phytophthora infestans*,2) we isolated two new sesquiterpenes, which were designated as oxyglutinosone (**1**) and epioxylubimin (**2**), respectively. The present paper describes the isolation and structure elucidation of these stress metabolites.

Neutral chloroform extracts (59 g), obtained from the diseased potato tubers (300 kg), were separated as described previously2) to give "lubimin fraction" (Fraction E,2) 4.7 g) and "oxylubimin fraction" (Fraction H,2) 5.8 g). The former was further purified by repeated chromatography to yield an oxyglutinosone and isolubimin-rich fraction (160 mg), with lubimin and epilubimin-rich fractions (174 and 110 mg), which on acetylation followed by preparative TLC over silica gel (Merck GF_{254}) afforded oxyglutinosone (**1**) and isolubimin3) (**3**) as the respective acetates (**1a**, 43 mg and **3a**, 37 mg). The latter fraction was likewise separated to give epioxylubimin (**2**, 294 mg) and oxylubimin4) (**4**, 415 mg) in pure state.

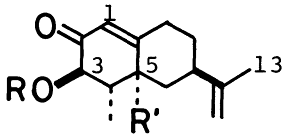
Oxyglutinosone acetate (**1a**), $C_{16}H_{22}O_4$, mp 99-101 °C, $[\alpha]_D$ +166° (EtOH), showed the following spectra:5) m/e 278 (M^+), 260, 218, and 178 (base); λ_{max}^{EtOH} 230 nm (ε 12100); $\nu_{max}^{CHCl_3}$ 3610, 3480, 1739, 1699, 1642, 1638, 1240, and 897 cm^{-1}; δ ($CDCl_3$) 1.10 (3H, d, J = 7), 1.75 and 2.19 (each 3H, s), 4.75 (2H, br s, W_H = 6), 5.39 (1H, d, J = 13, CHOAc), and 5.79 (1H, d, J = 1.5); δ (^{13}C) 71.6 (s), 109.6 (t), 122.7 (d), 148.4 (s), 162.7 (s), and 193.2 (s). These spectra, coupled with spin-decoupling studies on the spectra in the presence of the shift reagent [$Eu(dpm)_3$, 0.2-0.8 mol equiv], indicated the existence of the following structural unit; (■)-(CH_3)CH-C($OCOCH_3$)H-C(=O)-CH=(■) in **1a**, suggesting that **1** would be a 5-hydroxy derivative of glutinosone6) (**5**), a phytoalexin isolated from diseased tobacco leaves (*Nicotiana glutinosa*). This was confirmed as follows.

Rishitin2) (**6**) was converted into the 3-acetate7) (**6a**), which was oxidized with the Sharpless reagent to the 5α,10α-epoxide (**7**) (83%), mp 142-143 °C, $[\alpha]_D$ -14°; ν_{max}^{Nujol} 3480 (observed even in 0.0012 M CCl_4 soln), 1730, 1640, 1240, 1037, and 893 cm^{-1}; δ 3.11 (1H, d, J = 10, OH) (unchanged by dilution) and 3.69 [1H, do q, J = 10, 5, 5, and 5, CH(OH)]. The Collins oxidation of **7** followed by treatment with silica gel (Merck, 60 F_{254}) afforded hydroxy α,β-unsaturated ketone (54%), mp

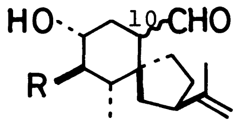
99-101 °C, $[\alpha]_D$ +153°, whose spectra (MS, UV, IR, and ^{1}H-NMR) were identical with those of 1a. Hydrolysis of 1a in a 1:1:2 mixture of triethylamine, water, and methanol (room temp, 3 h) followed by preparative TLC gave oxyglutinosone (1) (56%), $C_{14}H_{20}O_3$, $[\alpha]_D$ +130°; m/e 236 (M^+), 218, 200, and 178 (base); $\nu_{max}^{CHCl_3}$ 3560, 3440, 1682, 1643, and 890 cm^{-1}; δ 1.25 (3H, d, J = 6), 1.74 (3H, s, 13-H), 4.10 (1H, d, J = 12, 3-H), 4.73 (2H, m, W_H = 7), and 5.89 (1H, d, J = 1.5, 1-H).

Epioxylubimin (2), $C_{15}H_{24}O_3$, mp 123-124 °C, $[\alpha]_D$ -12.1°, showed the following spectra: m/e 252 (M^+), 234, 216, and 165 (base); ν_{max}^{Nujol} 3390, 3220, 1720, 1640, and 893 cm^{-1}; δ 1.06 (3H, d, J = 7), 1.75 (3H, s), 3.08 (1H, t, J = 9, 3-H), 3.47 (1H, do t, J = 4, 9, and 9), 4.77 (2H, s), and 9.87 (1H, s). These and ^{13}C-NMR spectra (δ 46.7, s), compared with those of 4, suggested that 2 would probably be a 10-epimer of 4. This was confirmed as follows. Treatment of 2 with base (4% KOH in MeOH, room temp, 1 h) gave a 3:2 mixture (92%) of 4 and 2, from which 4 (50% of the mixture), mp 83-85 °C, $[\alpha]_D$ +52.6°, could be isolated.

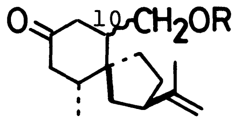
Isolubimin (3), oil, $[\alpha]_D$ +34.4°, obtained by hydrolysis of the acetate (3a), mp 49-51 °C, $[\alpha]_D$ +26.3°, was identical with that obtained from diseased potatoes by Stoessl et al.[3a] in IR, ^{1}H- and ^{13}C-NMR spectra.[5,8] Interestingly, epi-isolubimin (8), oil, which was prepared from epilubimin[9] (9) (hydride reduction of 9, partial acetylation, oxidation at C-2, and hydrolysis) and different clearly from 3, was practically the same as that obtained from healthy potatoes incubated with solavetivone by Kalan and Osman[3b] in MS and ^{1}H NMR spectra.[5]



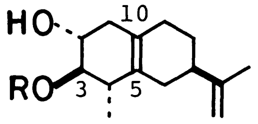
1 R=H, R'=OH
1a R=Ac, R'=OH
5 R=H, R'=H



2 10αH, R=OH
4 10βH, R=OH
9 10αH, R=H



3 10βH, R=H
3a 10βH, R=Ac
8 10αH, R=H



6 R=H
6a R=Ac
7 R=Ac, 5α,10α-O-

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